

Electronic Excitations from a Perturbative LDA+*GdW* Approach

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We discuss an efficient approach to excited electronic states within ab-initio many-body perturbation theory (MBPT). Quasiparticle corrections to density-functional theory result from the difference between metallic and non-metallic dielectric screening. They are evaluated as a small perturbation to the DFT-LDA band structure, rather than fully calculating the self energy and evaluating its difference from the exchange-correlation potential. The dielectric screening is described by a model, which applies to bulk crystals, as well as, to systems of reduced dimension, like molecules, surfaces, interfaces, and more. The approach also describes electron-hole interaction. The resulting electronic and optical spectra are slightly less accurate but much faster to calculate than a full MBPT calculation. We discuss results for bulk silicon and argon, for the Si(111)-(2×1) surface, the SiH₄ molecule, an argon-aluminum interface, and liquid argon.

I. INTRODUCTION

Many-body perturbation theory (MBPT) has become the state-of-the-art for excited states in electronic-structure theory.^{1,2} Starting from a density-functional theory (DFT) calculation, the *GW* method³ and its combination with the Bethe-Salpeter equation^{1,2} (BSE) allow to investigate the spectra of electrons, holes, and correlated electron-hole pairs. The great success of MBPT is based on the systematic incorporation of Coulomb interaction and polarization effects on all length scales, which is not considered in most other electronic-structure approaches. The significant computational cost of MBPT, however, still constitutes a major obstacle for the widespread use of the method. This holds in particular for larger-scale systems, like defects, hybrid systems, adsorbates, nanostructures, and others. In this paper we propose a dramatic reduction of the computational requirements of MBPT. As a result, the excellent precision of standard *GW* and *GW*+BSE calculations is slightly reduced, but instead the treatment of much larger systems becomes possible, thus allowing the investigation of spectroscopic features that might be inaccessible otherwise.

As key ingredient we exploit the observation that for many systems MBPT, when carried out by (wrongly) assuming *metallic dielectric screening*, approximately reproduces the band structure of the underlying DFT calculation (when employing the local-density approximation, LDA). This had already been observed by Wang and Pickett,⁴ as well as, by Gygi, Baldereschi, and Fiorentini^{5,6} and was subsequently exploited for model QP calculations for various materials.^{7,8} As illustration, Fig. 1 shows quasiparticle (QP) corrections for silicon (Si) and solid argon (Ar). The open circles (○) result from a conventional *GW* calculation (with standard RPA dielectric screening, “*GW*/RPA”), yielding the well-known opening of the band gap (by 0.7 eV for Si and 6.1 eV for Ar). The squares (□), on the other hand, come from *GW* calculations which employ *metallic* screening; these QP shifts are close to zero (at least for states near the Fermi level). The “metallic” dielectric screening is simulated

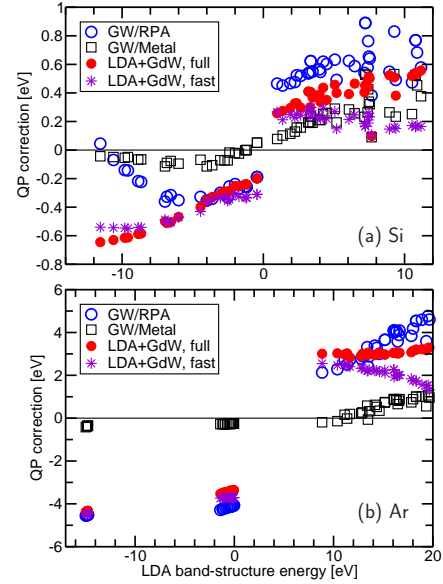


FIG. 1: (Color online) Quasiparticle corrections of (a) bulk Si and (b) bulk Ar. The open circles (○) denote standard *GW* data within RPA screening. The squares (□) result from a standard *GW* calculations, but based on a *metallic* dielectric model function (see text). The filled circles (●) result from the present LDA+*GdW* approach, employing the same basis and band-summation details as in the standard *GW* data. The asterisks (*, “fast”) result from LDA+*GdW* with 9 plane waves (15 plane waves for Ar) and 8 bands, only (see text).

by a dielectric model function.^{9–13} Here we use a model based on that of Bechstedt, Enderlein and Wischniewski,⁹ slightly modified (see Sec. II B) for broader applicability. Such models are controlled by a few parameters, most importantly by the macroscopic dielectric constant, ϵ_∞ . Setting $\epsilon_\infty \equiv \infty$ turns the screening into that of a metal.

If the *GW* method with metallic screening, W_{metal} , reproduces the DFT-LDA band structure, one can arrive at the true QP band structure by adding a self energy

$$\Delta\Sigma := iG_1(W - W_{\text{metal}}) = iG_1\Delta W \quad (1)$$

to the DFT-LDA Hamiltonian⁴⁻⁶. This procedure, which we label "LDA+ GdW " throughout the paper (see below for details), yields the filled circles (\bullet) in Fig. 1. These data agree fairly well with the GW /RPA data, at least in the important region near the fundamental gap; as a rule of thumb, we find that the gaps from $\Delta\Sigma := iG_1(W - W_{metal})$ agree with experiment to about 10 %, which largely corrects the DFT-LDA band-gap error of 30-50 %. Most importantly, long-range polarization effects are included, which is completely missing from the short-sighted DFT-LDA. This systematic improvement due to $\Delta\Sigma$ is much more important than plain agreement of band-structure data with experiment.

While Eq. (1) describes single-particle states of electrons and holes, a straight-forward extension to coupled electron-hole pairs and their optical response is easily possible by calculating the electron-hole interaction (from W) and solving the Bethe-Salpeter equation, BSE.^{1,2} Since the self-energy considered in this work is in principle still the one resulting from the GW approximation (GWA), the corresponding approximations to the electron-hole interaction are meaningful in the context of LDA+ GdW , as well.

As an important consequence of the above findings, the calculation of GW -like band structures via $\Delta\Sigma$ allows for a tremendous gain in numerical efficiency in four respects: (i) the use of model dielectric functions, (ii) small basis-set requirement, (iii) small band-summation requirement, and (iv) weak influence of dynamical effects. The underlying reason for all four issues is that the current approach calculates QP corrections to DFT-LDA as a *perturbation*. Most other GW implementations simply replace V_{xc} by Σ^{GW} , both of which are in the order of magnitude of ~ 10 eV or more. In order to get their difference to within 0.1 eV, the GW calculation must be carried out with numerical precision better than 1 %. Our present approach, on the other hand, starts directly at the QP *correction* (i.e., $\Delta\Sigma$), which is much smaller in magnitude (~ 1 eV) and much more robust. Here it is fully sufficient to evaluate all quantities to within 10 %, only, to achieve the same final numerical accuracy in the band structure.

The approach to be proposed in this paper is similar to the method by Gygi, Baldereschi and Fiorentini,^{5,6} who employed their perturbative GW method for the comprehensive analysis of bulk crystals. As a key difference to their approach, here we employ a different, more general model dielectric function which is flexible enough to also describe composite systems containing metals, non-metals, molecules, surfaces, interfaces, and more. As illustration, we discuss in this paper bulk materials, a semiconductor surface, a molecule, a metal-insulator junction, and a disordered insulator. In all cases our approach yields spectroscopic data of high quality (although slightly less accurate than the corresponding full GW or GW /BSE calculation), demonstrating an appealing combination of predictive power, broad applicability, and numerical efficiency.

The paper is organized as follows. In Sec. II we discuss the computational approach and the dielectric model function employed in this work. In Sec. III characteristic results for bulk silicon and bulk argon are discussed. Sec. IV presents results for more complicated systems, indicating the potential of the method. The paper is concluded by a summary in Sec. V.

II. THEORETICAL APPROACH

In this section we discuss the computational method used in this work, including its practical realization and underlying physical principles.

A. Perturbative quasiparticle corrections

Ab-initio quasiparticle (QP) band structures result from the electron self-energy operator $\Sigma(E)$. The state-of-the-art approach to Σ is given by Hedin's GW approximation,³ which is usually evaluated and employed on top of an underlying density-functional theory (DFT) calculation. The typical procedure employs DFT data to generate the single-particle Green function G_1 and the screened interaction W (usually within the random-phase approximation). Thereafter, the resulting self-energy operator $\Sigma = iG_1W$ replaces the DFT exchange-correlation potential, V_{xc} , arriving at a QP Hamiltonian of

$$\hat{H}^{QP} := \hat{H}^{DFT} + iG_1W - V_{xc} \quad (2)$$

This procedure is commonly labelled "many-body perturbation theory" (MBPT). However, this does *not* mean that Eq. (2) would be evaluated truly perturbatively in the sense that the smallness of the difference ($iG_1W - V_{xc}$) would be exploited. Instead, both terms, iG_1W and V_{xc} , are evaluated separately, taking their difference afterwards. The QP corrections are thus obtained as (small) differences between two (rather large) quantities, both of which have to be evaluated independently and with high precision. Simply speaking, in order to get their difference (often ~ 1 eV) to within 0.1 eV (which is the accuracy expected from MBPT), both iG_1W and V_{xc} (being of the order of ~ 10 eV or more) need to be evaluated with a precision of 1%. The underlying reason for this problem is the quite different conceptual origin of the two terms, which makes it difficult to formulate their difference in analytic terms.¹⁴

Fortunately, there does exist some pragmatic link between Σ and V_{xc} : The self energy of the homogeneous electron gas (as a function of the energy of a given state) is nearly constant (see Ref. 3) and thus nearly coincides with V_{xc} . [Note that this might not be truly fulfilled by approximations to Σ , like the GWA, which might suffer from offsets.] This behavior is reflected by the observation that in bulk metals, QP corrections (from GWA) to DFT-LDA band structures are very small.^{15,16} In other

words, DFT (at least within the local-density approximation, LDA) does contain correct spectral properties of the quasiparticles, at least for homogeneous systems. Within LDA, however, these spectral properties are by construction still those of the metallic system (jellium) from which the LDA exchange-correlation data originate, and this metallic behavior (in particular, metallic screening) is a built-in property of the exchange-correlation potential, even when applied to non-metallic systems. A generalization of this statement would imply that $V_{xc} \approx iG_1W_{metal}$ (provided that iG_1W is a good approximation to Σ) with the appropriate W_{metal} (i.e. metallic screening). In fact, GW studies employing metallic screening (including ours, see Fig. 1) confirm that $V_{xc}[n\mathbf{k}] \approx iG_1W_{metal}[n\mathbf{k}]$ for most electronic states $|n\mathbf{k}\rangle$.

Based on the working hypothesis that for non-homogeneous, non-metallic systems the largest difference to metallic behavior is the difference in *screening*, and employing $V_{xc} \approx iG_1W_{metal}$, one arrives at the QP Hamiltonian

$$\hat{H}^{QP} \approx \hat{H}^{DFT-LDA} + iG_1(W - W_{metal}) \quad , \quad (3)$$

in which $\Delta\Sigma = iG_1(W - W_{metal})$ acts as a self energy, yielding QP corrections (cf. Eq. (1)). The most important change to Eq. (2) is the fact that Eq. (3) no longer evaluates the difference between the self energies (given by iG_1W and V_{xc}), but the difference in screening: $(W - W_{metal})$. This difference is much simpler and faster to treat than the difference between self energies. Note that on the other hand, the final accuracy of the QP band structure might be less than 0.1 eV because the entire approach, although being much more efficient from a numerical point of view, is based on the assumption that $V_{xc} \approx iG_1W_{metal}$, meaning a further approximation in addition to the GW approximation. The assumption that $V_{xc} \approx iG_1W_{metal}$ should be checked carefully for each system class.

As discussed below, the use of Eq. (3) allows for several numerical simplifications (see Sec. IID), leading to a higher efficiency than conventional GW calculations, allowing to tackle more complex systems. One of the most important facilitations is the use of model dielectric functions (see next section) instead of calculating the screening within the random-phase approximation.

B. Model dielectric function

The calculation of the dielectric function within the random-phase approximation (RPA), which is the common procedure within MBPT, is one of the bottlenecks of the method. A simplified evaluation of the dielectric function is an important contribution to improving the efficiency of MBPT (even without the considerations of the previous section). For this reason model dielectric functions are sometimes employed to avoid the RPA.^{17–22} In the present context, the use of models is also mandatory for another reason: The key ingredient of the present

theory is the difference between the correct screening of the (non-metallic) system and its (hypothetical) metallic counterpart. This is only useful and well-defined if both types of screening result from the same approach, allowing to tune the screening from "correct" to "metallic" in a seamless manner. It is, however, unclear how the RPA could be used to simulate metallic behavior of a non-metallic system. An appropriate model is therefore a necessity of the current approach.

Examples are the models proposed by Bechstedt, Enderlein, Wischniewski, and Falter and by Levine, Hybertsen and Louie.^{9–13} We have tested these models in the present context and find that they yield essentially the same results as the ones to be discussed below. In their original form, however, these models have one significant disadvantage which may hinder their application to more complex systems: they were formulated for systems that are characterized by one common dielectric constant without spatial variation. This makes it difficult to employ them for systems in which the screening shows spatial variation, like interfaces, molecules, etc.

Instead we propose a model that is based on a combination of localized and delocalized quantities. The system may consist of N atoms (at positions τ_j) in a (periodically repeated) unit cell or supercell of volume V , with reciprocal lattice vectors \mathbf{G} . To each atom we attribute a static charge-density response $\chi^{(j)}$ (see below) and an effective volume V_j . The dielectric function of the whole system is then obtained as

$$\epsilon_{\mathbf{G},\mathbf{G}'}(\mathbf{q}) = \delta_{\mathbf{G},\mathbf{G}'} + \frac{1}{|\mathbf{q} + \mathbf{G}||\mathbf{q} + \mathbf{G}'|} \sum_{j=1}^N \frac{V_j}{V} \chi_{\mathbf{G},\mathbf{G}'}^{(j)}(\mathbf{q}) \quad . \quad (4)$$

The volume attributed to each atom controls the weight which the atom contributes to the response. The transformation from the charge-density response to the dielectric function further involves a convolution with the Coulomb interaction, i.e. the multiplication by $1/(|\mathbf{q} + \mathbf{G}||\mathbf{q} + \mathbf{G}'|)$ in Eq. (4). Note that we work with a symmetrised dielectric function.^{23,24}

It was suggested by Bechstedt *et al.* to describe the charge-density response of a (homogeneous) system with dielectric constant ϵ_∞ by⁹

$$f(Q; \bar{\rho}, \epsilon_\infty) = \left[\frac{1}{\epsilon_\infty - 1} + \frac{Q^2}{q_{TF}^2(\bar{\rho})} + \frac{Q^4}{\omega_P^2(\bar{\rho})} \right]^{-1} \quad (5)$$

where the Thomas-Fermi wave number q_{TF} and plasma frequency ω_P depend on the average electron density $\bar{\rho}$. Eq. (5) is related to the Lindhard dielectric function. In combination with Eq. (4) (for homogeneous systems, disregarding the summation over atoms), $\chi = Q^2 \cdot f$ would describe the dielectric function. In particular, for $Q \rightarrow 0$ one would correctly obtain $\epsilon(Q) \rightarrow \epsilon_\infty$ (if $\epsilon_\infty < \infty$, i.e. for non-metals) or $\epsilon(Q) \rightarrow 1 + q_{TF}^2/Q^2$ (if $\epsilon_\infty = \infty$, i.e. for metals), respectively. The generalization to *non*-homogeneous systems is less clear. While the large- Q behavior, which reflects the short-range reaction of electronic charge to

external fields on the sub-atomic length scale, appears realistic for non-homogeneous systems as well, the realistic incorporation of atomic-length-scale charge-density variation and of local fields (i.e. off-diagonal matrix elements of $\chi_{\mathbf{G},\mathbf{G}'}^{(j)}(\mathbf{q})$) is less clear.

Here we propose to model the charge-density response attributed to each atom by:

atom with metallic response:

$$\chi_{\mathbf{G},\mathbf{G}'}^{(j)}(\mathbf{q}) = \sqrt{f(|\mathbf{q} + \mathbf{G}|; \bar{\rho}_j, \infty) f(|\mathbf{q} + \mathbf{G}'|; \bar{\rho}_j, \infty)} \cdot |\mathbf{q} + \mathbf{G}| |\mathbf{q} + \mathbf{G}'| \cdot e^{-\gamma_j(\mathbf{G}' - \mathbf{G})^2} e^{i(\mathbf{G}' - \mathbf{G})\boldsymbol{\tau}_j} \quad (6)$$

atom with nonmetallic response:

$$\chi_{\mathbf{G},\mathbf{G}'}^{(j)}(\mathbf{q}) = \sqrt{f(|\mathbf{q} + \mathbf{G}|; \bar{\rho}_j, \epsilon_j) f(|\mathbf{q} + \mathbf{G}'|; \bar{\rho}_j, \epsilon_j)} \cdot (\mathbf{q} + \mathbf{G})(\mathbf{q} + \mathbf{G}') \cdot e^{-\gamma_j(\mathbf{G}' - \mathbf{G})^2} e^{i(\mathbf{G}' - \mathbf{G})\boldsymbol{\tau}_j} \quad (7)$$

In both cases, the factor $\sqrt{f(|\mathbf{q} + \mathbf{G}|) f(|\mathbf{q} + \mathbf{G}'|)}$ is a reasonable average of the large- Q behavior in directions $(\mathbf{q} + \mathbf{G})$ and $(\mathbf{q} + \mathbf{G}')$. The phase factor for each atom results from the position of the atom within the unit cell or supercell. The factor $\exp[-\gamma_j(\mathbf{G}' - \mathbf{G})^2]$ describes the spatial extent of the charge density of atom j . Without this factor (or with $\gamma_j \rightarrow 0$), the model describes a sharp point-charge-density response at position $\boldsymbol{\tau}_j$. With $\gamma_j \rightarrow \infty$ all local fields would be switched off, turning the model into that of a homogeneous system again. For a non-zero, finite value of γ_j , the factor $\exp[i(\mathbf{G}' - \mathbf{G})\boldsymbol{\tau}_j] \exp[-\gamma_j(\mathbf{G}' - \mathbf{G})^2]$ is the Fourier transform of a Gaussian-shaped charge density $\sim \exp[-(\mathbf{r} - \boldsymbol{\tau}_j)^2/(4\gamma_j)]$ centered at $\boldsymbol{\tau}_j$. In short, this means that the charge-density response is neither perfectly local (i.e., exactly at $\boldsymbol{\tau}_j$) nor completely delocalized (except for a truly homogeneous system, to be characterized by $\gamma_j \rightarrow \infty$). Instead, the charge-density response of an atom originates from its charge density (or at least from that of the polarizable electronic states), and its spatial form is included in the model. Correspondingly, $2\sqrt{\gamma_j}$ approximates the radius of the atom. It should be noted that the term $\exp[-\gamma_j(\mathbf{G}' - \mathbf{G})^2] \cdot \exp[i(\mathbf{G}' - \mathbf{G})\boldsymbol{\tau}_j]$ corresponds to the factor $\rho(\mathbf{G} - \mathbf{G}')/\rho(0)$ (i.e., Fourier transform of the charge density) in the model by Bechstedt *et al.*⁹ In our model the charge density of the entire system is approximated by a composition of atomic contributions with simplified shape.

A particular role is played by the factors $|\mathbf{q} + \mathbf{G}| |\mathbf{q} + \mathbf{G}'|$ (for metallic response) and $(\mathbf{q} + \mathbf{G}) \cdot (\mathbf{q} + \mathbf{G}')$ (for non-metallic response) in Eqs. (6) and (7). These factors reflect the qualitatively different origin of the response of metallic and non-metallic systems. For metals, long-range charge fluctuations and displacements are possible, resulting from intraband transitions near the Fermi level. Such displacements lead to charge accumulation at some atoms and charge depletion at others. Here our model assumes that such charge accumulation or depletion would basically show the same spatial structure as the original charge density of the atom (modeled by $\exp[-(\mathbf{r} - \boldsymbol{\tau}_j)^2/(4\gamma_j)]$), i.e. $\delta\rho_j(\mathbf{r}) \sim \rho_j(\mathbf{r})$.

The charge-density response of a non-metal, on the other hand, is of completely different origin. Here the response to an external field is mainly given by a short-range displacement of charge density from one side of the atom to the other, i.e. by a polarization of the atom. In many cases, this polarizability is dominated by transitions from s orbitals to p orbitals or vice versa. The spatial structure of such $s \leftrightarrow p$ polarizability is given by a factor $(\mathbf{r} - \boldsymbol{\tau}_j) \cdot (\mathbf{r}' - \boldsymbol{\tau}_j)$, leading to a factor of $(\mathbf{q} + \mathbf{G}) \cdot (\mathbf{q} + \mathbf{G}')$ in reciprocal space. Again, the additional factor $\exp[-(\mathbf{r} - \boldsymbol{\tau}_j)^2/(4\gamma_j)]$ (or its reciprocal-space counterpart) reflects the fact that the response comes from the whole atom (including some spatial extent) rather than from a single point.

The model can also be generalized to the case of anisotropic response, e.g. if an atom is embedded in a non-isotropic chemical environment, like in molecules, at surfaces, in sp^2 -bonded carbon, in atomic monolayers on a substrate, or similar. The same holds for materials with an anisotropic dielectric-constant tensor. In both cases, the response of each atom should be modeled with a direction-dependent dielectric-constant parameter $\epsilon_j(\hat{\mathbf{q}})$. Since such a situation can be expressed in terms of the three principal axes $\mathbf{n}^{(k)}$ and corresponding principal values $\epsilon^{(k)}$ of a 3×3 tensor (see next section for details), a straight-forward generalization of Eq. (7) is possible:

atom with nonmetallic response:

$$\chi_{\mathbf{G},\mathbf{G}'}^{(j)}(\mathbf{q}) = \sum_{k=1}^3 \sqrt{f(|\mathbf{q} + \mathbf{G}|; \bar{\rho}_j, \epsilon_j^{(k)}) f(|\mathbf{q} + \mathbf{G}'|; \bar{\rho}_j, \epsilon_j^{(k)})} \cdot [(\mathbf{q} + \mathbf{G})\mathbf{n}_j^{(k)}] \cdot [\mathbf{n}_j^{(k)}(\mathbf{q} + \mathbf{G}')] \cdot e^{-\gamma_j(\mathbf{G}' - \mathbf{G})^2} e^{i(\mathbf{G}' - \mathbf{G})\boldsymbol{\tau}_j} \quad (8)$$

One especially useful feature of the model proposed in this work is the possibility to combine metallic and non-metallic response in one system. This is particularly relevant for adsorbates on metallic substrates, for metal-insulator interfaces etc. Here our model simply allows to attribute metallic parameters (i.e., Eq. (6)) to some atoms and non-metallic parameters (i.e., Eqs. (7) or (8)) to others. For the construction of W_{metal} , finally, we simply take metallic response of all atoms (i.e., Eq. (6)). Apparently, for metals (or metallic regions) the dielectric function is the same in both cases.

C. Determination of the model parameters

The determination of the parameters is a particular task. Fortunately, the final use of the model for *differences* between metallic and non-metallic screening makes the entire approach insensitive to the actual choice of the parameters V_j , $\bar{\rho}_j$, and γ_j . Within this work, we simply attribute a realistic volume to each atom (for silicon, e.g., we choose $V_j = 20 \text{ \AA}^3$, which is the volume per atom of bulk Si), as well as a realistic valence electron number

(for silicon, apparently $N_j=4$). The average electron density $\bar{\rho}_j = N_j/V_j$ defines the Thomas-Fermi wave number $q_{TF,j}$ and plasma frequency $\omega_{P,j}$ for this atom, to be used in $f(Q)$. The parameter γ_j is obtained from least-square fitting of the atomic charge density by a Gaussian function. These parameters are used for both the metallic and the non-metallic response of atom j .

For non-metals one needs the dielectric-constant parameter ϵ_j (or the principal axes and values of the corresponding tensor for anisotropic situations). Such values can either be taken from experiment, or they are calculated for the particular system. One possibility is given by the evaluation of the small- \mathbf{q} limit of $\epsilon_{\mathbf{G}=0,\mathbf{G}'=0}(\mathbf{q})$ from the electrical-dipole operator applied to the inter-band transitions of the system, leading to a 3×3 tensor of

$$\epsilon_{ab} = \delta_{ab} + \sum_v \sum_c^{occ} \sum_{\mathbf{k}} \frac{\langle v\mathbf{k}|\hat{p}_a|\mathbf{c}\mathbf{k}\rangle \langle v\mathbf{k}|\hat{p}_b|\mathbf{c}\mathbf{k}\rangle^*}{(E_{\mathbf{c}\mathbf{k}} - E_{v\mathbf{k}})^3} \quad (9)$$

($a,b = x,y,z$) from which the principal axes and values can be evaluated. Note that Eq. (9) does not contain local-field effects. However, since the resulting ϵ_j enter our model *before* the inversion of $\epsilon_{\mathbf{G},\mathbf{G}'}(\mathbf{q})$ (which then leads to the local-field effects), the employment of local-field-free parameters is not a problem, but rather a requirement of the model.

In many systems the responses of the various atoms will differ from each other, leading to the question of distributing the results of Eq. (9) over the individual atoms. Here we propose to employ an atom-centered local-orbital basis for the calculation of the electronic states, $|n\mathbf{k}\rangle$. Such a basis allows to decompose the dipole matrix elements $\langle v\mathbf{k}|\hat{p}_a|\mathbf{c}\mathbf{k}\rangle$ into individual contributions of each atom j , i.e. one can focus on atom j and switch off the dipole strength of all other atoms. In this case Eq. (9) yields an individual result for each atom alone, allowing to find out the individual parameters of each atom in the system.

D. Numerical efficiency

As an important consequence of the above findings, the calculation of GW -like band structures via $\Delta\Sigma$ allows for a tremendous gain in numerical efficiency in four respects: (i) the use of model dielectric functions, (ii) small basis-set requirement, (iii) small band-summation requirement, and (iv) weak influence of dynamical effects. As mentioned, the underlying reason for all four issues is that the current approach calculates QP corrections to DFT-LDA as a *perturbation*. The four issues of efficiency (i)-(iv) deserve detailed discussion.

(i) The advantage of working with a dielectric model function rather than employing the random-phase approximation has already been pointed out in the last section. In particular, the perturbative idea of Eqs. (1) and (3) *requires* a model, even beyond the issue of numerical efficiency.

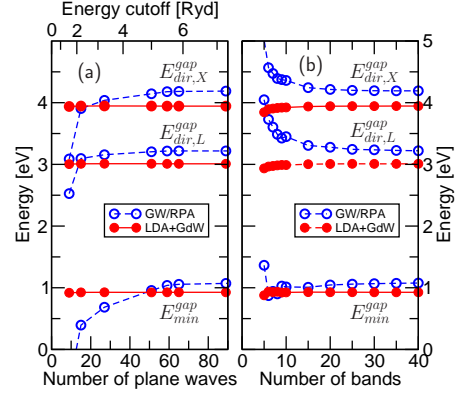


FIG. 2: (Color online) Gap energies of Si (indirect minimum gap, direct gap at L , and direct gap at X), calculated within a full GW calculation (employing RPA screening) and within the present $LDA+GdW$ scheme. (a) Dependence of the gap energies on the plane-wave basis representation of W (or $(W - W_{metal})$, respectively), as controlled by the energy cutoff (upper axis). (b) Dependence of the gap energies on the number of bands considered in the band summation inside the self-energy operator. [Note that this does not refer to the number of bands considered in the calculation of the RPA screening.]

(ii) The basis-set requirements for $(W - W_{metal})$ are much weaker than for W alone for two reasons: (ii.1) Within full GW the bare-exchange contribution requires a large basis for convergence. In our present approach, on the other hand, the bare-exchange effects are the same in GW and GW_{metal} and thus cancel each other. (ii.2) While both W and W_{metal} are structured in real space, their *difference* is a rather smooth function and converges with very few basis functions. Fig. 2 a shows representative gap energies of Si as a function of the plane-wave basis size used for W . Full GW requires about 60 plane waves (~ 5 Ryd cutoff) for reasonable accuracy while the $LDA+GdW$ data are already converged with 9 plane waves (~ 1.4 Ryd). Similarly, basis-set convergence for Ar requires cutoff energies of about 15 Ryd for GWA, but only about 2 Ryd for $LDA+GdW$.

(iii) The band summation in $\Delta\Sigma$ is less demanding than in a full GW calculation because the influence of the higher conduction bands (via G_1) is weak. This is shown in Fig. 2 b. The use of about as many conduction bands as valence bands is sufficient for $LDA+GdW$ (at least for states near the gap), while conventional GW calculations are usually performed with at least about 10 times more conduction than valence bands. This behavior again results from the smooth spatial structure of $(W - W_{metal})$. To summarize statements (ii) and (iii), Fig. 1 includes data from 1.4 Ryd cutoff (2.0 Ryd for Ar) and four conduction bands in G_1 as asterisks (*, "fast"). The agreement with the converged $LDA+GdW$ data shown by (•) is sufficient, except for higher-energy states.

(iv) Within conventional GW calculations, the correlation part of Σ (which is subject to dynamical effects)

can be as large as 5-10 eV. Our $\Delta\Sigma$, on the other hand, is much smaller in magnitude and thus much less sensitive to dynamical effects. This allows to treat $\Delta\Sigma$ on the level of the static COHSEX approximation,²⁵ which we employ in all LDA+*GdW* calculations in this paper. Note that this does not apply to the *GW*/RPA and *GW*/Metal reference calculations in this paper, all of which include dynamical effects by using a plasmon-pole approximation. In those cases, the generalization of the static model of Sec. II B to a dynamic dielectric function is realized by evaluating the *f*-sum rule.²⁶

III. RESULTS FOR BULK SILICON AND ARGON

The QP corrections to DFT-LDA for bulk Si and Ar are compiled in Fig. 1. As discussed above, full *GW* calculations using a metallic *W* yield QP corrections close to zero, opening the possibility of perturbative LDA+*GdW* as proposed in Sec. II. In fact, the LDA+*GdW* data are close to those of a full *GW* calculation employing correct, non-metallic screening from RPA (open circles). There are, however, some deviations (related to the LDA+*GdW* method as such, and also to the dielectric model function). For Si, for example, the lowest valence bands observe very small QP corrections within *GW*/RPA, but significant negative QP corrections within LDA+*GdW*. Furthermore, the QP corrections for the conduction bands appear to be less accurately reproduced by LDA+*GdW* than for the upper valence bands. Additional deviations are observed for the "fast" LDA+*GdW* approach (at minimal basis-set and band-summation specification), in particular for the higher conduction bands. These details notwithstanding, we can conclude that LDA+*GdW* yields sufficient accuracy if one is interested in states near the fundamental gap. Furthermore, systematic deviations between LDA+*GdW* and *GW*/RPA can be expected to be similar in bulk systems and other, more complicated systems of the same material (like, e.g., surfaces, nanostructured systems, interfaces, etc.). LDA+*GdW* will allow for systematic comparison between the spectral data of such systems.

The quite reliable LDA+*GdW* band structures can be employed to yield reasonable optical spectra, as well. To this end we include electron-hole interaction on the level of the Bethe-Salpeter equation.² The interaction kernel is calculated with the same (non-metallic) dielectric model function and same basis as the band structure. One exception is the unscreened exchange interaction between electrons and holes (originating from the Hartree potential) which may require a larger energy cutoff than the screened interaction and must be treated separately. Its calculation is relatively cheap and does not affect the efficiency of our approach.

Fig. 3 shows the macroscopic imaginary dielectric function $\epsilon_2(\omega)$ of bulk Si and Ar. The thin dotted curves

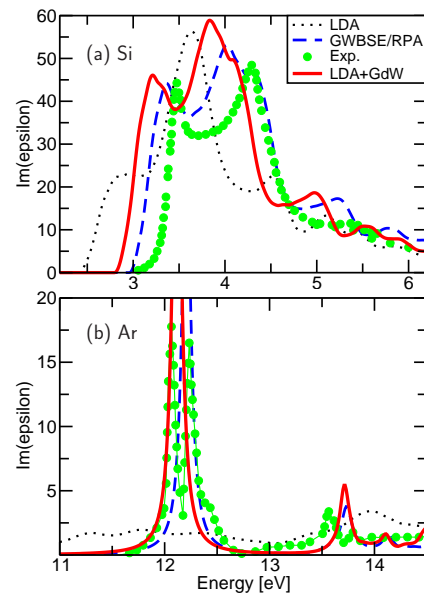


FIG. 3: (Color online) Optical spectrum (imaginary part of macroscopic dielectric function) of bulk Si and of bulk Ar. Experimental data are from Ref. 27–29 (Si) and from Ref. 30 (Ar). Note that spin-orbit coupling (leading to the measured double-peak structure of the Ar exciton) is not included in our calculations.

display the spectrum from the uncorrelated LDA interband transitions, which is usually qualitatively and quantitatively wrong (in particular for insulators, like Ar). The dashed lines are reference data from a full *GW*+BSE/RPA calculation, which can be considered as the state-of-the-art approach to $\epsilon_2(\omega)$. The solid lines display our current results, including the drastic numerical simplification ("fast") as outlined above. In comparison with the *GW*+BSE/RPA data and with experiment, the LDA+*GdW* data are very gratifying. They correctly yield the two characteristic peaks (at 3-3.5 eV and at 4-4.5 eV) of the Si spectrum. For Ar, we obtain an exciton peak at 12.2 eV (*GW*+BSE/RPA) or 12.1 eV (LDA+*GdW*), respectively. In experiment, the spin-orbit interaction (neglected in our present work) splits the exciton into two peaks at 12.0 and 12.2 eV. Furthermore, a second excitonic peak is found near 13.5 eV. The slight deviations between LDA+*GdW* and the *GW*+BSE/RPA reference data mostly result from corresponding deviations in the band structure. Note that for Ar, the agreement is even better than can be expected from our current approach. Most importantly, the differences between LDA+*GdW* and *GW*+BSE/RPA are not significantly larger than the deviations from experiment, thus advertising LDA+*GdW* as a useful alternative. Compared to the LDA interband spectrum, a tremendous improvement of explanatory power is achieved.

[eV]	LDA	GW/Metal	GW/RPA	LDA+ GdW	Exp.
bulk E_{min}^{gap}	0.49	0.51	1.10	0.95	1.17 ^a
$D_{up}(J)$	0.0	0.0	0.0	0.0	0.0 ^b
$D_{down}(J)$	0.4	0.4	0.7	0.8	0.7 ^c

^aRef. 31 ^bRef. 32 ^cRef. 33

TABLE I: Characteristic band-structure data for the Si(111)-(2×1) surface, which is dominated by two dangling-bond states derived from the Pandey-chain termination. At the J point of the surface Brillouin zone the related bands (occupied D_{up} and unoccupied D_{down} state) are closest to each other and define the surface band gap.³⁴

[eV]	LDA	GW/Metal	$GW/\text{BSE}/\text{RPA}$	LDA+ GdW	Exp. [35]
E_{LOMO}	-13.5	-14.0	-17.8	-17.3	
E_{HOMO}	-8.4	-9.0	-12.5	-11.8	-12.6
E_{LUMO}	-0.6	-0.2	0.4	0.6	
$\Omega_{triplet}$			8.0	7.6	
$\Omega_{singlet}$			9.0	8.3	8.8

TABLE II: Spectral data of the SiH₄ molecule, which is dominated by quantum confinement and shows the typical electronic excitations of a small molecule.

IV. RESULTS FOR MORE COMPLEX SYSTEMS

We have tested the LDA+ GdW approach for a number of inhomogeneous systems, starting from the bulk materials (Si and Ar) discussed above.

A. Si(111)-(2×1) surface and silane molecule

Based on the experience with bulk silicon, we investigate two prototypical systems of silicon in reduced dimensions, i.e. the SiH₄ molecule and the Pandey-chain terminated Si(111)-(2×1) surface. Both systems have been intensively studied in theory and experiment (see, e.g., Ref. 34 and 36 and references therein). Here we focus on their electronic structure within the present LDA+ GdW approach.

In the case of the Si(111)-(2×1) we focus on the band structure of the Pandey-chain derived dangling-bond states.^{32,33,37–42} The dangling bonds result from the lower coordination (three-fold instead of four-fold) of the Pandey-chain atoms, leading to one occupied and one empty state within the bulk band gap.³⁴ These two bands constitute one of the most intensively studied surface electronic structures. At the J point of the surface Brillouin zone the two bands are well separated from the silicon bulk states and define the surface band gap. Within LDA, this gap suffers from the same type of band-gap underestimation as all semiconductor systems. Here we observe a value of 0.4 eV, much smaller than the experimental result of 0.7 eV from a combination of direct and inverse photoemission (see Tab. I).^{32,33}

Within GW/RPA , the surface bands are significantly shifted and result in very good agreement with the measured data.^{32–34,40,41} It is most gratifying to see that this behavior is also given by the present LDA+ GdW approach, which yields a surface gap energy of 0.8 eV. This good agreement also holds for the absolute energetic position (with respect to the bulk band structure). Both for the occupied and for the empty band, the data from GW/RPA , LDA+ GdW , and experiment all agree to within 0.1 eV.

The screening properties for this calculation have been obtained from the approach as outlined in Sec. II C, yielding individual screening properties for each atom. Here we find that the charge-density response of the surface atoms is slightly larger than that of the bulk-like atoms in the center of the slab. The response of the bulk-like atoms agrees with that of a true bulk calculation to within 10 percent. At the surface, on the other hand, the smaller surface band gap, the π -conjugated nature of the Pandey chain, and the vicinity of the vacuum lead to an anisotropic response. Perpendicular to the surface, the response is reduced by about 25 % (leading to a dielectric-constant parameter of about $\epsilon_j^{(\perp)}=9$ instead of the bulk value of $\epsilon_j=12$). Parallel to the Pandey chain, on the other hand, the response is doubled to $\epsilon_j^{(\parallel)}=24$.

As another, even more extreme case for silicon in reduced dimension, we discuss the silane molecule (SiH₄).^{35,36,43} Its electronic structure is dominated by quantum confinement, leading to much larger band gaps and QP corrections than for extended semiconductors. All relevant data are compiled in Tab. II. Compared to the LDA data, the occupied states (i.e. the lowest occupied molecular orbital, LOMO, and (three-fold degenerate) highest occupied molecular orbital, HOMO), are lowered in energy by more than 4 eV. Here the current LDA+ GdW approach reproduces these QP shifts to within about 0.5 eV. The lowest unoccupied molecular orbital (LUMO), on the other hand, is shifted to higher energies by 1.0 eV (GW/RPA) or 1.2 eV (LDA+ GdW), respectively. Based on these reliable data for single-particle states, LDA+ GdW also yields reasonable data for charge-neutral electron-hole excitations (see Tab. II). Here we take the lowest-energy singlet and triplet excitation as representative examples. While $GW+\text{BSE}$ within RPA yields data in excellent agreement with experiment³⁵ and with other many-body and quantum-chemical methods,³⁶ the data from LDA+ GdW show slightly lower excitation energies. The deviations are in the order of 0.5 eV and correspond to the differences in the band-structure energy of the HOMO state, for which LDA+ GdW yields a slightly too high value. Nevertheless, in light of the huge QP corrections and very strong electron-hole interaction of about 5 eV in SiH₄, we consider the accuracy of LDA+ GdW (i.e. yielding QP shifts and electron-hole binding to within 20 %) extremely gratifying.

Similar to the case of the Si(111)-(2×1) surface, screening in SiH₄ differs significantly from that of bulk silicon.

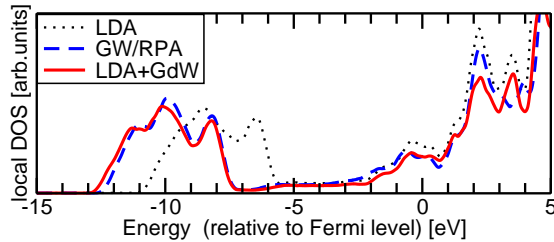


FIG. 4: (Color online) Local density of states in a mono-layer of Ar, combined with a 5-layer aluminium(001) slab in a heterostructure.

The much larger gap reduces the charge-density response strongly. Our approach of locally evaluating the density-response contribution of each atom yields an isotropic response of the silicon atom to be described by $\epsilon_j=3.75$ (and similar results for the H atoms), i.e. weaker than bulk Si by a factor of 4. Such strong reduction for chemically passivated silicon in confined geometries was already found earlier.⁴⁴

We close this section by mentioning that for both systems, Si(111)-(2×1) and SiH₄, the underlying reason for the success of the LDA+*GdW* approach is again given by the reproduction of the DFT-LDA band-structure data when metallic screening is employed in a full *GW* calculation. The corresponding data are included in Tab. I and Tab. II. In particular for the Si(111)-(2×1) surface, this mandatory condition for the applicability of LDA+*GdW* is nearly exactly fulfilled. For the SiH₄ molecule some difference of the order of 0.5 eV are found. Considering the massive deviation of this system from a homogeneous metal, even this agreement to within 0.5 eV is an amazing result.

B. Argon systems

Spatially varying dielectric response is also present in metal-insulator heterostructures. As an example Fig. 4 shows the single-particle spectrum of a periodic heterostructure composed of five atomic layers (10 Å) of aluminium and one atomic layer (3 Å) of argon, stacked along the Al(001) direction. This system combines metallic screening in Al with insulating behavior in Ar, which has significant consequences on the QP energetics.^{45–48} Here we focus on the local density of states (LDOS) in the Ar monolayer. The LDOS between -12 eV and -6 eV results from the upper valence states of Ar (3*p*), while the LDOS above 2 eV comes from the Ar conduction bands, with increasing admixture of Al states at higher energy. The LDOS inside the Ar band gap (-6 eV to +2 eV) results from spill-out of Al states into the Ar layer. The most interesting feature is the rather small QP correction of the argon states, which (in *GW/RPA*) amounts to -1.7 eV (+0.2 eV) for the upper valence (lower conduction) states, yielding a total correction of 1.9 eV for

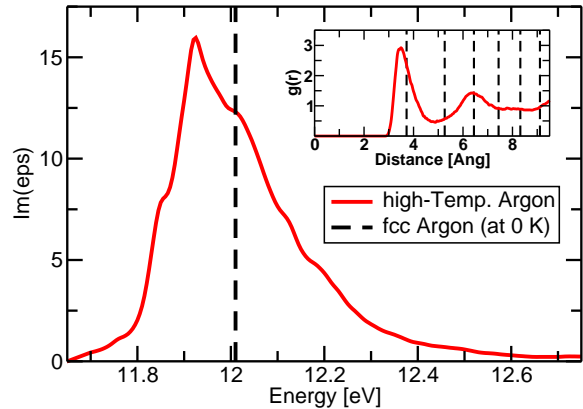


FIG. 5: (Color online) Optical spectrum of the excitons in non-crystalline argon (from molecular dynamics of 64 atoms at 300 Kelvin, at the solid-argon density — see text), resulting from the current LDA+*GdW* approach. The dashed line indicates the position of the exciton in the periodic crystal. The inset shows the Ar-Ar pair-correlation function of the MD simulation.

the fundamental gap of Ar. In bulk Ar, on the other hand, the gap-edge states observe QP shifts of -4.1 eV and +2.0 eV, yielding a gap correction of 6.1 eV (cf. Fig. 1). The presence of metallic screening in the immediate neighborhood significantly weakens the QP shifts due to image-state effects,^{45–48} both for holes and for electrons (by about 2 eV each). It is most gratifying to see that in our LDA+*GdW* approach (again with a plane-wave cut-off of 2 Ryd), the spatial set-up of the dielectric model function (cf. Eq. (4)) reproduces these effects. Here LDA+*GdW* yields QP shifts of -1.8 eV and +0.2 eV for the band-edge states and a gap correction of +2.0 eV, compared to the Ar bulk data (see Fig. 1) of -3.5 eV, +2.8 eV, and +6.3 eV. We conclude that the LDA+*GdW* approach is a suitable method for addressing electronic properties of metal-nonmetal junctions.

As a last example for the potential of our method, Fig. 5 shows the exciton spectrum of non-crystalline argon. At zero temperature argon forms a periodic face-centered cubic (fcc) lattice, which can easily be treated by MBPT (see Sec. II), leading to the results as discussed in Sec. III. For this periodic solid the exciton yields a sharp line (except for dynamical broadening effects from self trapping or similar, that are completely neglected here). This changes in the case of non-periodic argon, like in its liquid or amorphous state. Such systems may be described by sufficiently large supercells. At present we investigate the spectra resulting from a 64-atom cell (consisting of 4×4×4 fcc unit cells) and exploit its spectral features from the Γ point of the supercell, only. For the periodic fcc crystal this yields an exciton at 12.01 eV excitation energy (slightly lower than the value reported in Sec. III, which was obtained from the standard fcc unit cell containing one atom, and 500 *k*-points in the BSE). Within this configuration (which is computationally

ally much more demanding than a simple one-atom-fcc calculation and is extremely demanding for the standard $GW+BSE$ Hamiltonian) the spectrum of liquids or amorphous systems can be evaluated. At present we simply consider argon at its solid-state density (for comparison sake), but heated to 300 Kelvin (although this is an unrealistic high temperature for argon at this density). We perform a constant-temperature molecular-dynamics simulation (using a simple Lennard-Jones interatomic potential), leading to the Ar-Ar pair-correlation function shown in the inset of Fig. 5. Such a simulation is certainly not fully realistic in terms of describing liquid or amorphous systems; nonetheless it yields structural elements that may very well be present in liquids. The pair-correlation function clearly exhibits structures beyond harmonic vibrations (like, e.g. the vanishing of the second-nearest-neighbor peak at 5.3 Å), thus prohibiting a perturbative electron-phonon interaction treatment in the evaluation of the spectrum. Instead, our $LDA+GdW$ approach (averaged over 20 snapshots of the MD run) easily allows to evaluate the spectrum. The data shown in Fig. 5 clearly demonstrate three important features: (i) the exciton line is significantly broadened, (ii) the broadening is asymmetric, leading to substantial non-zero amplitude well above the exciton energy, and (iii) the maximum of the peak is at lower energy than in the periodic system. The third feature is related to the fact that

in the pair-correlation function, the first maximum also occurs at smaller distance (3.4 Å) than the fcc nearest-neighbor-distance (3.7 Å), which is a consequence of the anharmonicity of the Ar-Ar interatomic potential.

V. SUMMARY

In summary, we have discussed an extremely efficient modification of standard many-body perturbation theory (GW method plus Bethe-Salpeter equation). Based on the observation that metallic screening in the GW method approximately reproduces the DFT-LDA band structure (which should be checked for each material), quasiparticle (QP) corrections to DFT-LDA are obtained in a truly perturbative approach at minimal cost, provided that the dielectric screening can be described by an appropriate model. The resulting QP band structures and optical spectra (including electron-hole interaction) are slightly less accurate than those from conventional $GW+BSE$, but they include all Coulomb-interaction effects (like screening, electron-hole binding etc.) in a physically correct way, allowing to systematically investigate excitations beyond DFT and beyond the computational limits of conventional MBPT.

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